

## PHYSICAL METHODS OF INVESTIGATION

# Pressure and Temperature Dependences in $p$ -ZnAs<sub>2</sub> at High Pressures

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**Abstract**—Kinetic effects in  $p$ -ZnAs<sub>2</sub> were measured at hydrostatic ( $P \leq 9$  GPa) and quasi-hydrostatic (to  $P \leq 50$  GPa) pressures on pressure buildup and depressurization. A conclusion on the occurrence of two phase transitions was made: I–II at  $P = 9$ –15 GPa and II–III at  $P = 30$ –35 GPa. Based on the temperature dependences of electrical resistance, it was shown that the conductivity is determined by activation mechanisms in a temperature range of 250–400 K; in this case, the activation energy changed with temperature and pressure. The pressure dependences of the activation energy and the coefficient  $R_0$ , which characterizes the mobility, concentration, and effective mass of carriers, were calculated.

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Zinc diarsenide (ZnAs<sub>2</sub>) is a II–V semiconductor compound, which crystallizes in the monoclinic system [1] and has the band-gap energy  $E_g \approx 1$  eV. The structure peculiarity of ZnAs<sub>2</sub> is the presence of bands between As atoms, which form zigzag chains elongated along the  $c$  axis (crystallographic orientation [100]), together with Zn–As bonds; this peculiarity is responsible for the significant anisotropy of electrical and optical properties. Along with the high transparency of ZnAs<sub>2</sub> in a wide range of wavelengths in the IR region (1.4–20  $\mu\text{m}$ ), the possibility of developing a solid-state laser on its basis is of the greatest interest for practical use [2]. Induced emission at a wavelength of 1.235  $\mu\text{m}$  was obtained from ZnAs<sub>2</sub> single crystals upon electronic pumping.

Among the publications dedicated to the study of ZnAs<sub>2</sub> at high pressures, the work by Clark and Pistorius [3] is well known; they measured the resistivity of polycrystalline ZnAs<sub>2</sub> in Bridgman anvils at pressures to 11 GPa at 25°C. However, the I–II phase transition to  $P \leq 11$  GPa was not discovered by resistometric measurements. Therefore, it was of interest to determine resistivity and Hall effect in the single-crystal samples of ZnAs<sub>2</sub>.

## EXPERIMENTAL

The measurements were performed at hydrostatic (to  $P \leq 9$  GPa) and quasi-hydrostatic (to  $P \leq 50$  GPa) pressures. The hydrostatic pressure was generated by a compression unit with a stress of 500 ton-force. The

dependences of resistivity  $\rho$  and Hall coefficient  $R_H$  were measured simultaneously in a Toroid anvil/truncated-hemisphere-type high pressure apparatus (HPA), which was placed in a multiturn solenoid with the magnetic field intensity  $H \leq 300$  kA/m [4]. The sizes of the samples were  $3 \times 0.8 \times 0.8$  mm. A mixture of ethanol–methanol in a ratio of 4 : 1, which is hydrostatic to the pressures  $P \leq 9$  GPa, was used as a pressure fluid. The resistivity, Hall coefficient, and pressure measurement errors were  $\pm 3$ , 3.5, and 3%, respectively. The measurement procedure was described in more detail elsewhere [4, 5].

Pressure from 15 to 50 GPa was produced with the use of a high-pressure chamber (HPC) with anvils of the plane–rounded cone type [6, 7], made from the carbonado-type synthetic polycrystalline diamonds. These anvils are good electric conductors; this fact makes it possible to measure the pressure and temperature dependences of the resistance of a sample placed between the anvils, which are used as contacts. This procedure allowed us to cyclically change pressure applied to the sample. This makes it possible not only to study conductivity changes under changes in pressure but also to analyze possible changes in the sample structure based on irreversible changes in electrical properties (the prehistory of the sample). The measurements were performed in a temperature range of 77–400 K.

Pressure was determined from the formula  $P = AF/\pi a^2$ , where  $F$  is the applied force,  $a$  is the contact radius, and  $A$  is an empirical coefficient (in our case,

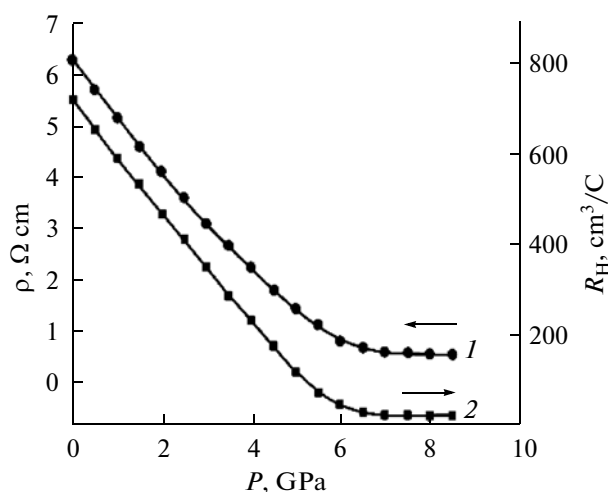


Fig. 1. The pressure dependence of the (1) electrical resistivity and (2) Hall coefficient of  $\text{ZnAs}_2$ .

$A = 1.51$ ). This method for determining pressure was tested with a significant group of different materials over wide temperature and pressure ranges. The measurement procedure was described in detail elsewhere [7].

## RESULTS AND DISCUSSION

The single crystals of  $p\text{-ZnAs}_2$  cut along the crystallographic direction [001] had the following parameters:  $\rho = 6.3 \, \Omega \, \text{cm}$  and  $|R_H| = 725 \, \text{cm}^3/\text{C}$  at  $25^\circ\text{C}$ . The resistivity and Hall coefficient were measured at hydrostatic pressures to  $P \leq 9 \, \text{GPa}$ . Figure 1 shows that the resistivity (curve 1) decreased by an order of magnitude as the pressure was increased in the range of  $P = 0\text{--}7 \, \text{GPa}$ . The resistivity remained almost unchanged

in the range of pressures  $P = 7\text{--}9 \, \text{GPa}$ . The results of Hall coefficient measurements (curve 2) show that  $R_H$  decreased by two orders of magnitude with pressure in the range of pressures from 0 to 7 GPa, and then it reached a saturation level. In the saturation region, the concentration of carriers was  $\approx 3 \times 10^{18} \, \text{cm}^{-3}$  and the mobility was  $\approx 30 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ . It is likely that higher pressures are required for detecting phase transformations.

The subsequent measurements were continued in the HPC of the plane–rounded cone type. A comparison between the shapes of  $\rho(P)$  curves obtained at a hydrostatic pressure (Fig. 1) and in the diamond chambers (Fig. 2) allowed us to assume that it is most likely that an extended phase transition occurred in the range of pressures  $P = 9\text{--}15 \, \text{GPa}$ .

As the pressure was further increased, the resistance nonmonotonically decreased and a II–III phase transition was observed at  $P \approx 30\text{--}35 \, \text{GPa}$  (Fig. 2). Three regions with different pressure resistances can be recognized in the pressure dependence (Fig. 2). From the experimental results, it follows that a high-pressure phase appears at high pressures ( $P \approx 30\text{--}35 \, \text{GPa}$ ), and this phase remains stable at a normal pressure; that is, the process is irreversible. As the pressure was decreased after reaching its maximum value, the pressure dependence of resistance did not coincide with the pressure dependence for the initial material. The resistance of the sample became lower than the initial value. In the subsequent cycles of increasing and decreasing pressure, the resistance of the sample changed with a pressure hysteresis; in this case, its value at a normal pressure remained almost constant.

Figure 3 shows the pressure dependences of thermopower at room temperature for the first and fifth cycles. Because of the high resistance, reliable mea-

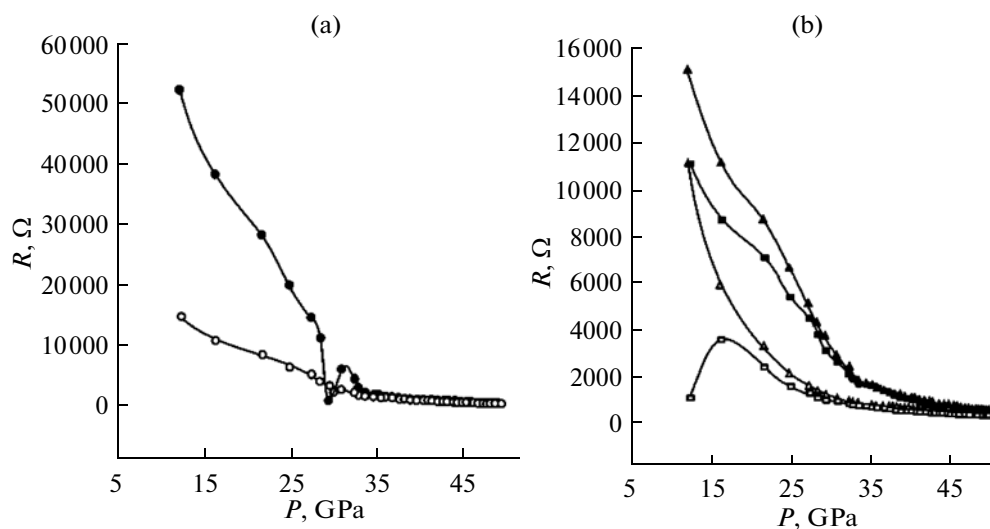
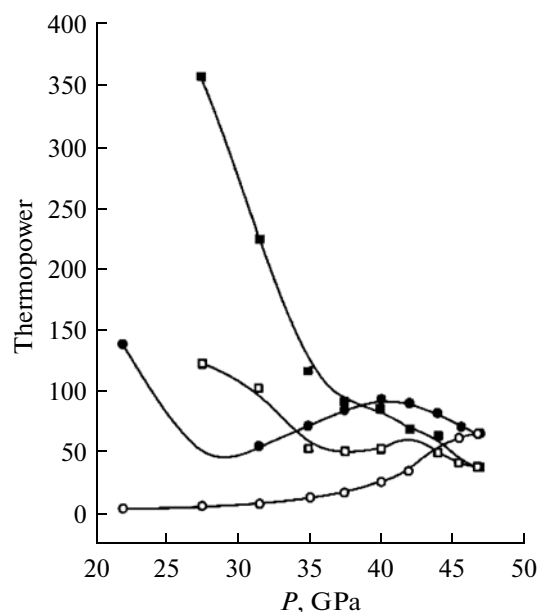
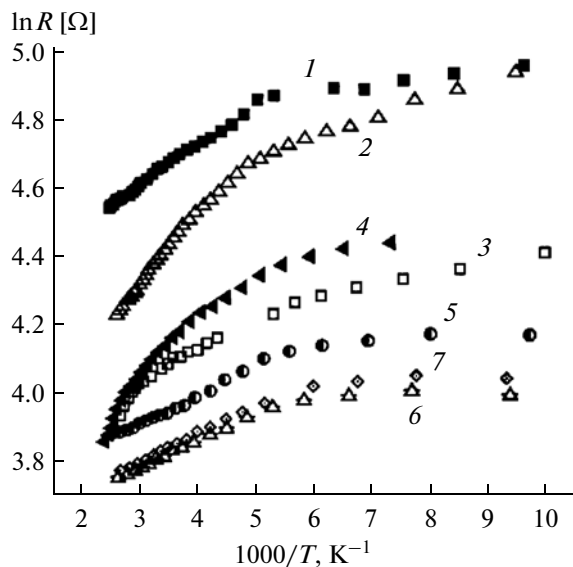


Fig. 2. The pressure dependence of the resistance of  $\text{ZnAs}_2$  at room temperature (filled and open points refer to pressure buildup and release, respectively): (a) the first cycle of pressure application and (b) the subsequent cycles of pressurization.



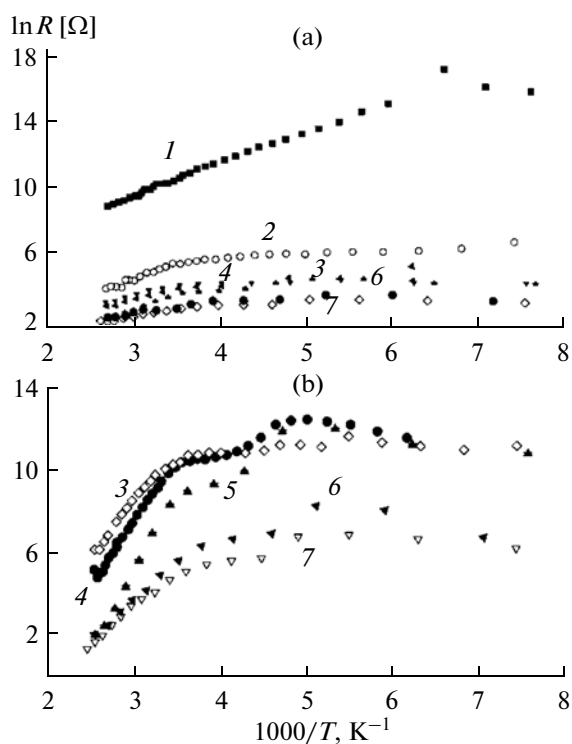
**Fig. 3.** The pressure dependence of thermopower at room temperature (filled and open points refer to pressure buildup and release, respectively; circles and squares indicate the first and fifth cycle, respectively).



**Fig. 5.** The temperature dependence of the electrical resistance of  $\text{ZnAs}_2$  (subjected to pressure treatment in the initial state) under the subsequent action of the following pressures, GPa: (1) 22, (2) 27, (3) 35, (4) 40, (5) 44, (6) 45.5, and (7) 47.

measurements can be performed only in the pressure range of 25–50 GPa. At a pressure of 40 GPa, the concentration of charge carriers evaluated from the thermopower was  $\sim 2 \times 10^{21} \text{ cm}^{-3}$ ; that is, metallic conductivity took place.

Because the initial phase and the high-pressure phase have different electrophysical characteristics,



**Fig. 4.** The temperature dependence of the electrical resistance of  $\text{ZnAs}_2$  (in the initial unpressurized state) under the subsequent action of the following pressures, GPa: (1) 22, (2) 27, (3) 31.5, (4) 35, (5) 40, (6) 44, and (7) 45.5.

we studied the temperature dependences of the resistance of  $\text{ZnAs}_2$  on the primary and subsequent pressurization.

Figure 4 shows the temperature dependences that correspond to the unpressurized sample. Figure 4b shows an expanded portion of the graph given in Fig. 4a. In the region of 250–400 K, the resistance exhibits an activation character; there are transitional and low-temperature regions, in which the resistance does almost not depend on temperature.

The temperature dependences of the resistance of the pressurized sample are similar to those described above (Fig. 5); however, the range of resistance changes is much smaller. The resistance does not depend on temperature at low temperatures.

Based on these data, we calculated the activation energy and the coefficient  $R_0$ , which characterizes the mobility, concentration, and effective mass of charge carriers depending on pressure (Fig. 6), using the following equation:

$$R = R_0 e^{E_a/kT}. \quad (1)$$

Curves 1 and 4 in Fig. 6 correspond to the activation energy of conductivity and the coefficient  $R_0$ , respectively, for the unpressurized sample. It is evident that a maximum activation energy was observed at pressures of  $\sim 40$  GPa, and the coefficient  $R_0$  was char-

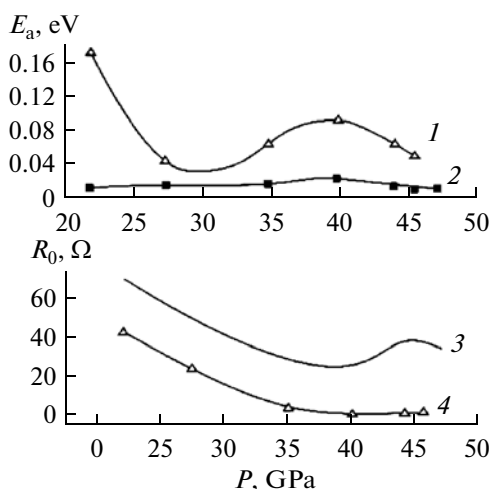


Fig. 6. The pressure dependence of the activation energy and coefficient  $R_0$ .

acterized by no singularities. The repeated pressure treatment (curves 2 and 3) led to a significant decrease in the maximum activation energy and the appearance of a singularity in the graph of  $R_0$ .

Thus, we were the first to simultaneously measure resistivity, Hall coefficient, and thermopower in zinc diarsenide at a hydrostatic pressure of up to 9 GPa (Toroid HPA) and a quasi-hydrostatic pressure of up to 50 GPa (HPC with an anvil of the plane–rounded cone type). The comparative analysis of the shapes of the hydrostatic curves of the pressure dependences  $\rho(P)$  and the quasi-hydrostatic curves of  $R(P)$  allowed us to assume the occurrence of the first structural phase transition in the range of the pressures  $P = 9\text{--}15$  GPa. Based on the data of  $R(P)$  to 50 GPa, we concluded that the second structural phase transition occurred at  $P = 30\text{--}35$  GPa. From the pressure dependence of

thermopower at  $P \sim 40$  GPa, we estimated the concentration of charge carriers at  $\sim 2 \times 10^{21} \text{ cm}^{-3}$ ; that is, metallic conductivity took place.

We found that the electrophysical characteristics of  $\text{ZnAs}_2$  underwent irreversible changes at the pressures  $P \leq 50$  GPa. We calculated the pressure dependence, activation energy, and coefficient  $R_0$ , which characterize the mobility, concentration, and effective mass of charge carriers, respectively, from the temperature dependences of  $R(P)$ .

## ACKNOWLEDGMENTS

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